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Synthesis of MFI zeolites with improved crystallization rate and mesoporosity in the presence of CO_2-in-water emulsions

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ABSTRACT

In this work, we demonstrate a novel and efficient route for fast crystallization of MFI zeolites of silicalite-1 and ZSM-5 with enhanced silica condensation in the presence of CO_2-in-water microemulsions. Compared to the conventional synthesis method, this new technique needs a very short time for the crystallization of MFI zeolites (4–8 h) in the presence of compressed CO_2. Furthermore, the synthesis of MFI zeolites containing mesoporosity (mesoporous MFI zeolites) under compressed CO_2 condition does not require any organotemplate, which is of great economic importance to industrial application. Interestingly, ZSM-5 synthesized in the presence of compressed CO_2 possessed uniform chain-like crystal morphology, while silicalite-1 synthesized in the presence of compressed CO_2 exhibited monodispersed crystals as characterized by scanning electron microscopy (SEM). We have extended the CO_2-in-water microemulsions route to synthesize other zeolites such as TS-1, Beta and Y. This newly developed method opens a new avenue for the fast synthesis of template-free mesoporous zeolites.

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1. Introduction

Zeolites have been widely applied in oil and petrochemical catalysis as solid acid catalysts and functional materials [1–5], but their relatively small and uniform micropores strongly influence the mass transfer of reactants and products thus reduce the catalytic conversion of bulky molecules. One solution for this problem is to prepare mesoporous zeolites. Successful examples for synthesizing mesoporous zeolites are the use of mesoscale templates such as organic–inorganic hybrid surfactants [6], silylated polymer [7], and mesoscale cationic polymers [8]. These mesoporous zeolites are more catalytically active than conventional zeolites due to the fast mass transfer of reactants and products [9–12]. However, the use of these mesoporous zeolites on an industrial scale is rather limited, because of the high cost of the organic template for the formation of mesoporosity and the complexity of the synthetic procedures. Therefore, the challenges associated with synthesizing porous materials mean that new methods of preparing known zeolites continue to be of great importance [13–15].

Supercritical or compressed CO_2 has received much attention in recent years because of its availability, low cost, nonflammability and low toxicity. Compressed CO_2 has been widely used in different fields, such as extraction and fractionation [16], chemical reactions and material science [17,18], controlling the stability of reverse micelles [19], induction of nanoemulsions [20], creating microemulsion with CO_2 as continuous phase [21–23], changing membrane fluidity and melting point of liposome system [24], and tuning the properties of organic solvents [25]. Emulsion templating is useful for the preparation of highly porous materials, such as organic polymers [26–28], inorganic materials [29–32], and inorganic–organic composites [33]. To date, there are a few examples of successful use of compressed CO_2 in the preparation of porous materials with amorphous walls [34–38]. For examples, supercritical CO_2 is used as swelling agent to tailor the pore sizes of hexagonal mesoporous silicas [34,35]; porous semiconducting gels and aerogels are obtained from the supercritical drying with carbon dioxide [36]; mesoporous silica hollow spheres are prepared from CO_2-in-water (C/W) emulsion templating in the presence of non-ionic block copolymers [37]. Hierarchical strings of mesoporous silica spheroids were synthesized at the interface of CO_2–water emulsion systems by utilizing Na_2CO_3 additive and the structure-directing surfactant of Brij 97 [38].

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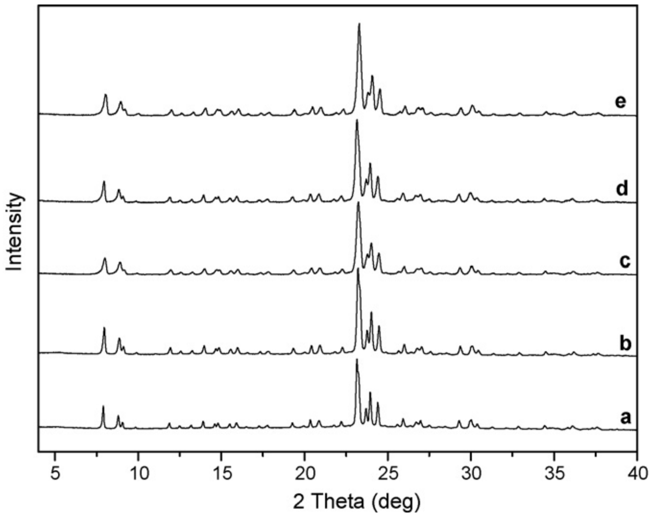

Fig. 1. XRD patterns of (a) silicalite-1-S crystallized for 4 h in the presence of compressed CO_2, (b) silicalite-1-S crystallized for 8 h in the presence of compressed CO_2, (c) conventional silicalite-1 crystallized for 96 h in the absence of compressed CO_2, (d) ZSM-5-S crystallized for 8 h in the presence of compressed CO_2 and (e) conventional ZSM-5 crystallized for 88 h in the absence of compressed CO_2.

Up to now, no crystalline zeolites were prepared by using compressed CO_2 either as solvent or template. Herein we demonstrate the first efficient compressed CO_2 route for synthesizing MFI zeolites including silicalite-1 and ZSM-5. Compressed CO_2 route takes shorter time for the crystallization of MFI zeolites compared to the conventional synthesis. Moreover, mesoporosity could be formed in crystalline MFI zeolites without using any mesoscale organotemplate, and the mesopore volume could be increased significantly by increasing CO_2 pressure. This formation of mesoporosity in MFI zeolite synthesized under compressed CO_2 condition is apparently related to the presence of CO_2-in-water emulsions and foams as templates, which are stabilized by silica species during the synthesis.

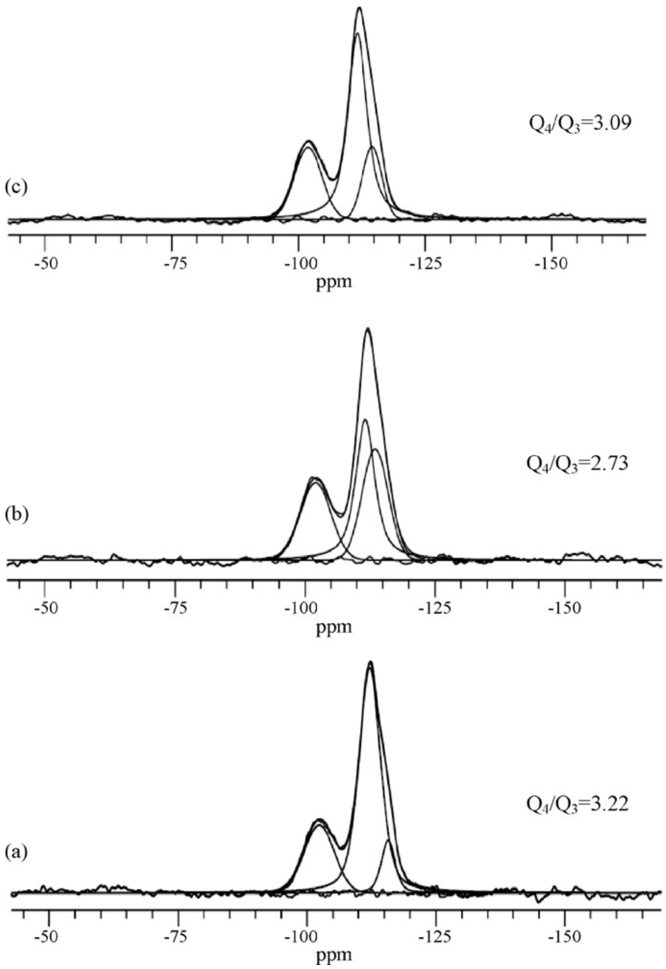

Fig. 2. ^{29}Si NMR spectra of (a) silicalite-1-S crystallized for 8 h in the presence of compressed CO_2, (b) conventional silicalite-1 crystallized for 8 h in the absence of compressed CO_2 and (c) conventional silicalite-1 crystallized for 96 h in the absence of compressed CO_2.

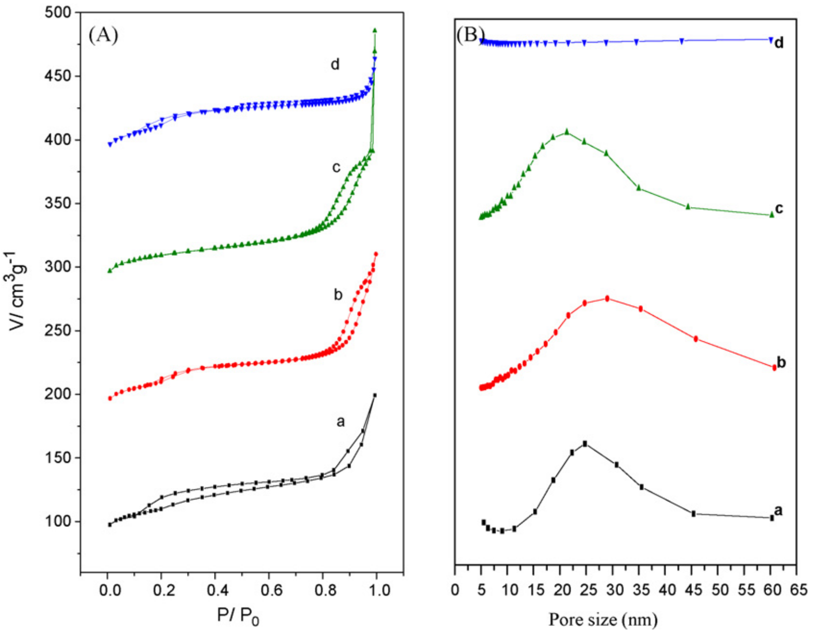

Fig. 3. (A) N_2 isotherms and (B) pore size distributions for (a) silicalite-1-S-8 MPa crystallized in the presence of compressed CO_2, (b) ZSM-5-S-8 MPa crystallized in the presence of compressed CO_2 at 8 MPa, (c) ZSM-5-S-15 MPa crystallized in the presence of compressed CO_2 at 15 MPa and (d) ZSM-5-N_2-8 MPa crystallized under compressed N_2 at 8 MPa. The isotherms for (b), (c) and (d) are offset by 100, 200 and 300 $cm^3\ g^{-1}$, respectively, for clarity.

Table 1
Textural parameters of various MFI zeolites.

Sample	S[a], m^2/g	V_{total}[b], cm^3/g	V_{meso}[c], cm^3/g	D_{meso}[d], nm
Silicalite-1-S-4 h–8 MPa	305	0.22	0.13	10–40
Silicalite-1-S-8 h–8 MPa	364	0.23	0.11	10–40
Conventional silicalite-1-96 h	362	0.18	0.06	–
ZSM-5-S-8 h–8 MPa	315	0.25	0.14	10–40
ZSM-5-S-8 h–15 MPa	327	0.35	0.24	10–40
ZSM-5-N_2-24 h–8 MPa	334	0.16	0.08	–

[a] BET surface area.

[b] Total pore volume at $P/P_0 = 0.95$.

[c] Pore volume estimated by *t*-plot method.

[d] Pore size distribution obtained from BJH analysis by adsorption branch.

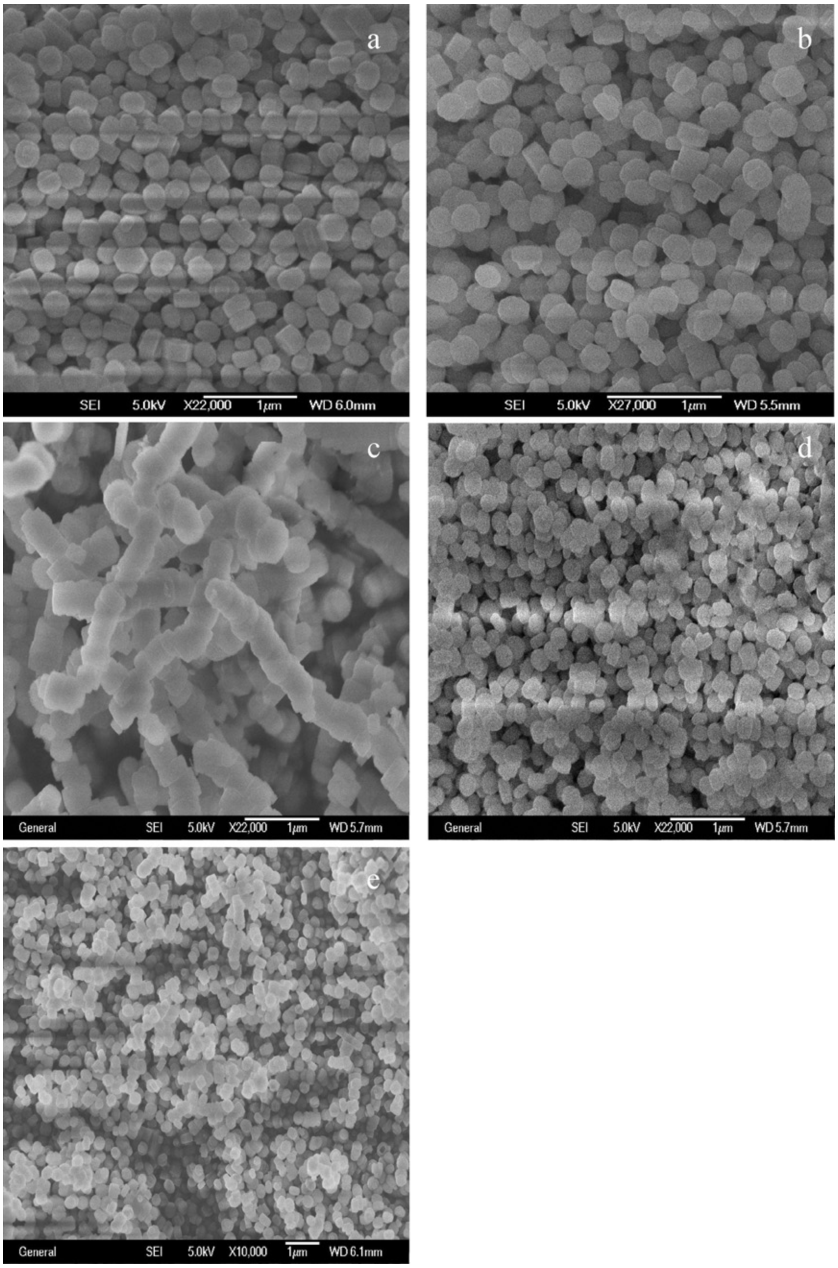

Fig. 4. SEM images of (a) silicalite-1-S crystallized for 8 h in the presence of compressed CO_2, (b) conventional synthesis of silicalite-1 crystallized for 96 h in the absence of compressed CO_2, (c) ZSM-5-S crystallized for 8 h in the presence of compressed CO_2, (d) conventional synthesis of ZSM-5 crystallized for 88 h in the absence of compressed CO_2 and (e) ZSM-5 synthesized for 24 h under N_2 atmosphere condition.

2. Experimental

2.1. Synthesis of MFI zeolites in the presence of compressed CO_2

The synthesis of silicalite-1 zeolite in the presence of compressed CO_2 was as follows: first, 6.25 mL of tetraethyl orthosilicate (TEOS), 10 mL of tetrapropylammonium hydroxide (TPAOH, 10.7 wt%) and 1.5 mL of NaOH aqueous solution (1 M) were mixed at room temperature. After stirring for 8 h, the mixture became a clear solution (molar composition of SiO_2:Na_2O:TPAOH:H_2O at 1:0.04:0.48:190) which was then transferred into 50 mL stainless steel autoclave. Then the autoclave was pressurized with CO_2 up to 8 MPa with high-pressure liquid pump and the reactants were crystallized at 150 °C for 4–96 h. The solid products were separated by filtration, dried at room temperature and calcined at 550 °C for 4 h. This sample was designated as silicalite-1-S.

The synthesis of ZSM-5 zeolites in the presence of compressed CO_2 designated as ZSM-5-S, was obtained from the molar ratio of SiO_2:Al_2O_3:Na_2O:TPAOH:H_2O at 1:0.0055–0.022:0.04:0.48:190 with aluminum isopropoxide as Al source at 150 °C as above. For comparison, conventional silicalite-1 and ZSM-5 zeolites were synthesized under the same conditions as those for silicalite-1-S and ZSM-5-S except for the absence of CO_2.

2.2. Phase behavior studies

The phase behavior of the CO_2-in-water emulsions was observed in 80 mL view cell. In a typical experiment, appropriate amounts of TEOS, TPAOH, and NaOH aqueous solution were added into the reactor in order to create the same conditions as those in the 50 mL reactor, and then replaced the air in the view cell by CO_2. After that, the contents were heated up to the desired temperature. After thermal equilibrium had been reached, the stirrer was started and CO_2 was charged into the cell slowly. The emulsions were observed after the stirring was stopped.

2.3. Characterizations of silicalite-1-S and ZSM-5-S

X-ray diffraction data (XRD) were collected on a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation. Nitrogen isotherms were measured using a Micromeritics ASAP 2010M system. The samples were degassed for 10 h at 300 °C before the measurement. Scanning electron microscopy (SEM) experiments were performed on JEOL electron microscopes (FE-JSM6700, Japan). Transmission electron microscopy (TEM) experiments were performed on a Philips CM 200 LaB6 operating at 200 kV and a JEM 3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. ^{29}Si MAS NMR spectra were carried out on a Varian Infinity plus-400 spectrometer fitting the sample in a 7 mm ZrO_2 rotor, spinning at 4 kHz with the number of scans being 308 and a collection time of 25.6 min. The Dmfit software was employed for deconvolution using fitted Gaussian–Lorentzian line shapes [39].

3. Results and discussion

In the presence of compressed CO_2, silicalite-1 and ZSM-5 zeolites with various Si/Al ratios, designated as silicalite-1-S and ZSM-5-S, respectively, were synthesized from silicate or aluminosilicate gel at 150 °C for 4–96 h. As observed from X-ray diffraction (XRD), the crystallization of silicalite-1-S and ZSM-5-S in the presence of compressed CO_2 condition takes very short time (4–8 h, Fig. 1a, b and d), compared with conventional syntheses of silicalite-1 and ZSM-5 with similar crystallinity (88–96 h, Fig. 1c and e). Thus these syntheses in the presence of compressed CO_2 are very favorable for the enhancement of the crystallization rate of MFI zeolites, which might be attributed to the carbonate species, formed from hydration of CO_2, acting as efficient promoters for the crystallization of MFI zeolites [40,41]. The improved crystallization rate was also confirmed by ^{29}Si MAS NMR technique (Fig. 2). As-synthesized silicalite-1-S with crystallization time for 8 h exhibits the ratio of fully condensed Q^4 silica units (−112 ppm) [42,43] to incompletely cross-linked Q^3 (−102 ppm) at 3.22 (Fig. 2a). In contrast, as-synthesized conventional silicalite-1 with crystallization time for 96 h shows lower Q^4/Q^3 ratio at 3.09 (Fig. 2c), indicating the carbon dioxide medium favours the silica condensation.

Nitrogen isotherm of silicalite-1-S synthesized for 8 h in the presence of CO_2 condition (Fig. 3A) exhibits three steps: the uptake below $P/P_0 = 0.02$, which is due to the filling of micropores; the hysteresis loop at relative pressure around $P/P_0 = 0.2$ and the uptake in the P/P_0 range of 0.6–0.95. The hysteresis loop observed in the relatively low pressure (0.2) is not associated with any pore filling but is possibly related to a phase transition of the liquid-like nitrogen confined in silicalite-1-S channels from a disordered to a more ordered solid-like state [44,45]. The hysteresis loop at relatively high pressure (0.6–0.95) is assigned to the presence of hierarchical mesopores [6–8,46–48]. Correspondingly, the sample mesopore size distribution is estimated at about 10–40 nm by applying a BJH method (Fig. 3B). Similarly, ZSM-5-S zeolites synthesized for 8 h under CO_2 condition (Fig. 3A-b and c) also exhibit hysteresis loops at relative pressure around $P/P_0 = 0.8–0.95$ associated with hierarchical mesopores. In contrast, there is no obvious hysteresis loop at relative pressure around $P/P_0 = 0.8–0.95$ over ZSM-5 zeolite synthesized under N_2 at the pressure of 8 MPa (Fig. 3A-d). These results indicate that the formation of mesoporosity in MFI zeolites is strongly related to the use of compressed CO_2 condition. The textural properties of various MFI zeolites are summarized in Table 1. When the pressure of CO_2 condition increased from 8 MPa to 15 MPa, pore volume in ZSM-5-S remarkably increased from 0.25 to 0.35 cm^3/g, confirming that compressed CO_2 is a key factor for the formation of mesoporosity. Recently, the introduction of mesoporosity in zeolite crystals by templating has received much attention due to the fast mass transfer of reactants and products. Successful examples for synthesizing mesoporous zeolites are the use of mesoscale templates [6–8]. However, in this work, we show the synthesis of mesoporous MFI zeolites using pressurized CO_2 but without mesoscale organotemplate. This new process could be cost-effective and environmentally benign because no organic mesoporous templates are used during synthesis.

Scanning electron microscopy (SEM) images (Fig. 4) of MFI zeolites exhibit the morphology of crystalline phases. Interestingly, silicalite-1-S shows monodispersed crystals (Fig. 4a), while ZSM-5-S gives chain-like crystal morphology (Fig. 4c). However, ZSM-5 synthesized under N_2 atmosphere at 8 MPa exhibited a monodispersed crystal morphology (Fig. 4e), which suggests that carbon dioxide played an important role in the morphology control.

Transmission electron microscopy (TEM) image of silicalite-1-S also clearly confirms the presence of uniform crystals (Fig. 5a). HRTEM image (Fig. 5b) clearly shows mesopores in silicalite-1-S crystals. The formation of mesoporosity in silicalite-1-S synthesized in the presence of compressed CO_2 condition is apparently related to the presence of CO_2-in-water emulsions and foams as templates, which are stabilized by silica species during the synthesis [49,50]. It is also suggested that the ethanol produced by the hydrolysis of TPAOH favors the formation of CO_2-in-water emulsion [49]. In order to verify the presence of CO_2-in-water emulsions in our synthetic system, the phase behaviors of the starting silica gels were observed by means of a see-through autoclave (Fig. 6). The droplets could not be observed for the starting silica gels in the absence of CO_2 (Fig. 6a). However, there existed obvious small droplets of CO_2 when a certain amount of carbon dioxide was charged into the autoclave. Furthermore, with the increasing of the CO_2 pressure and crystallization time, the droplets of CO_2 became

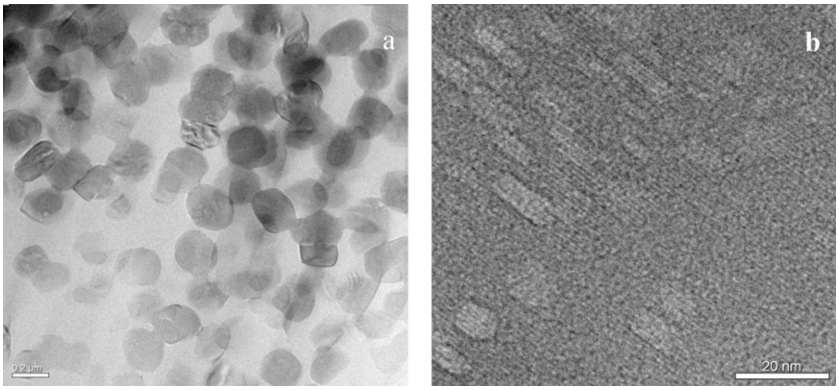

Fig. 5. (a) TEM image and (b) HR TEM image of silicalite-1-S crystallized for 8 h in the presence of compressed CO_2.

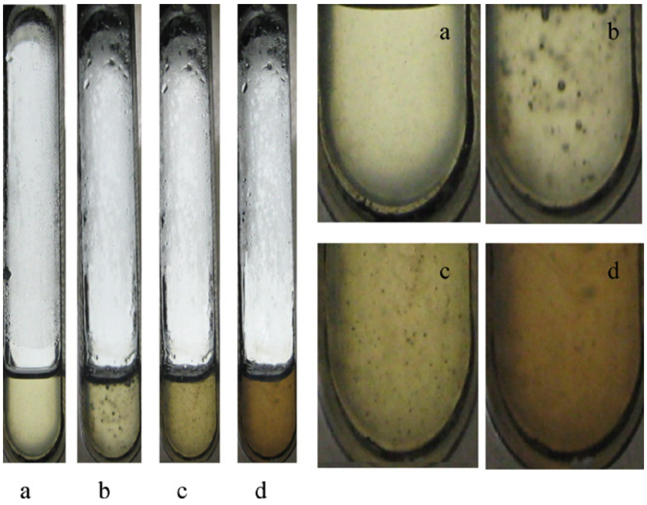

Fig. 6. Photographs of the phase behavior of starting silica gels (a) in the absence of compressed CO_2, (b) in the presence of CO_2 at 3 MPa, (c) in the presence of CO_2 at 5 MPa and (d) in the presence of CO_2 at 8 MPa.

smaller and smaller, or even invisible to the naked eye (Fig. 6b–d). It is proposed that the crystallization of MFI zeolites most probably proceeds in the aqueous phase, where compressed CO_2 dissolves in the form of an emulsion, which acts as the mesoporous template. After the CO_2 is depressurized, the mesopore is introduced into the zeolite crystal during the zeolite crystallization. Porous materials synthesized from such CO_2-in-water emulsions have been reported by others [51–55]. Other factors such as pH value of the reaction gel might play a crucial role in the synthesis of mesoporous MFI zeolite. The pH of starting silica gel used here was about 12.26 but decreased to 8.08 after crystallization in the presence of compressed CO_2. Lowering of pH resulted from CO_2 dissolved in water with partial ionization to form acid ($H_2O + CO_2 = H^+ + HCO_3^{-1}$).

4. Conclusion

In summary, we have developed a novel and facile synthesis route for mesoporous MFI zeolites. The use of compressed CO_2 leads to the fast crystallization of zeolite by enhanced silica condensation. Moreover, mesoporosity was formed in these zeolites without using organic mesoporous templates. The mesopores are introduced into the zeolite crystal by CO_2-in-water emulsions, which apparently acted as the mesoporous template. This route was also extended to synthesize other zeolites such as TS-1, Beta and Y. This method opens a new avenue for the fast synthesis of mesoporous zeolites without organic mesoporous templates.

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